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## Pulsed NMR by Tone-Burst Generation

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## Pulsed NMR by ToneBurst Generation

D. C. Look and D. R. Locker

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at 297°, 343°, and 398°K.<sup>8</sup> We found difficulty in obtaining reproducible data at dry-ice temperature and suspect that poor thermal contact was responsible for the earlier low value.

The lack of any deviation in the Arrhenius plot clearly indicates that below 729°K there is no contribution from the abstraction reaction. This is not surprising in view of the high pre-exponential factor measured for the addition reaction. For if we visualize the fastest possible abstraction reaction consistent with the endothermicity,<sup>9</sup> then its rate only becomes equal to that of the addition at 2500°K, and at 700°K, it is slower than the addition by a factor of 250. Thus, it is clear that the addition reaction must be the major pathway for removal of atomic oxygen by acetylene in high-temperature oxidation.

Its substitution for the abstraction reaction in the oxidation mechanism has several attractive features: (i) The over-all oxidation stoichiometry can be maintained by assuming only that methylene reacts predominantly with molecular oxygen. (ii) The strong dependence of the oxidation rate on oxygen concentration and the weak dependence on acetylene concentration is explained since the addition reaction rate constant is faster than that for the reaction of atomic hydrogen with oxygen<sup>10</sup> by a factor of 8 at 1500°K and by a factor of 3 at 2000°K. (iii) The addition reaction is only 2–3 times slower than an estimate, based upon the value of several rate constants that have since been slightly revised, of the rate of removal of acetylene by atomic oxygen in flames.<sup>11</sup> (iv) It explains the similarity in pattern and yield of chemiluminescence and chemi-ionization that is found in both the oxidation and in the addition reaction.

An interesting consequence of this modified oxidation mechanism is that both CH<sub>2</sub> and C<sub>2</sub>H are primary chain carriers. Since chemi-ionization is known to be second order in chain carrier concentration<sup>2</sup> and since C<sub>3</sub>H<sub>3</sub><sup>+</sup> is known to be an important chemi-ion, the possibility that it arises from CH<sub>2</sub> + C<sub>2</sub>H → C<sub>3</sub>H<sub>3</sub><sup>+</sup> cannot be overlooked.

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<sup>1</sup> J. N. Bradley and G. B. Kistiakowsky, *J. Chem. Phys.* **36**, 1707 (1962).

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<sup>9</sup>  $k = 2 \times 10^{14} \exp(-14 \text{ kcal}/RT) \text{ cm}^3 \text{ mole}^{-1} \text{ sec}^{-1}$ .

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<sup>11</sup> C. P. Fenimore and G. W. Jones, *J. Chem. Phys.* **39**, 1514 (1963).

## Pulsed NMR by Tone-Burst Generation

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(Received 23 October 1968)

Using a tone-burst generator (TBG) it is possible to do pulsed nuclear magnetic resonance (NMR) on an otherwise unmodified, wide-line, continuous-wave spectrometer. Furthermore, manual or electronic triggering of the generator provides a sequence of pulses, and the spin-lattice relaxation time ( $T_1$ ) may be determined from the resulting sequence of signals, according to known formulas.<sup>1</sup>

Specifically, we have applied a General Radio Model 1396B tone-burst generator to a Varian Model V-4200B wide-line NMR spectrometer. The TBG may be connected directly between the rf transmitter and the cross-coil probe, giving about 0.1-G rf field strength at 2 MHz, strong enough for work in liquids. For stronger rf fields we have used an IFI model 500A wide-band amplifier. Balancing out the leakage between the transmitter and receiver coils is accomplished in the usual manner. The free-induction decays (FID's) are recorded from an oscilloscope or time-averaging computer.

Presently, the operating frequency is limited to 2 MHz since this model TBG has an upper frequency limit of 2 MHz which is the lower limit of the spectrometer. Another limitation, without instrument modification, is the receiver blocking time, about 150  $\mu\text{sec}$ ; thus, the spin-spin relaxation time,  $T_2$ , must be a few hundred microseconds or greater, implying a linewidth of a few tenths of a gauss or less.

There are advantages in using a sequence of pulses of angle  $\theta < 90^\circ$ , started by manual or electronic triggering of the TBG. The resulting sequence of FID's shown in Fig. 1 contains all the information necessary for the determination of  $T_1$  and, if desired for signal-to-noise improvement, many sequences may be added in a time-averaging computer, triggered at the beginning of each sequence. This experiment is similar to the field tone-burst modulation technique<sup>1</sup> used in cw NMR spectroscopy and the mathematical analysis is equivalent. Separating the pulse sequences by about  $4T_1$  and letting the resulting amplitudes be designated by  $M_0, M_1, M_2, \dots, M_n, \dots$ , we have<sup>1</sup>

$$M_n = M_0 \times \frac{1 - \exp(-\tau/T_1) [1 - X(1-X)^n \exp(-n\tau/T_1)]}{1 - (1-X) \exp(-\tau/T_1)}, \quad (1)$$

where  $X$  is the amount of saturation given by  $X = 1 - \cos\theta$ ,  $0 < \theta < \pi$ . After many pulses the amplitude

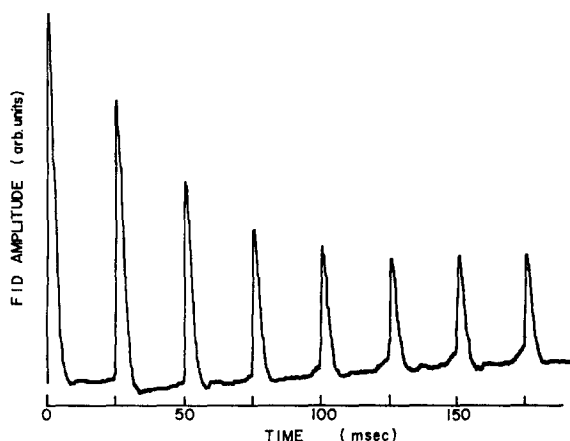


FIG. 1. A sequence of free induction decays in  $\text{Mn}^{2+}$ -doped  $\text{H}_2\text{O}$  after spin-system equilibrium (about  $4T_1$ 's). The 2-MHz pulses, not visible because of probe balance, are about 35  $\mu\text{sec}$  long and are spaced 25 msec apart. As explained in the text,  $T_1$  is calculated from the amplitudes and spacing. The above recorder tracing is the output of a time-averaging computer in which 30 such sequences have been added.

reaches a constant value,

$$M_\infty = M_0 \frac{1 - \exp(-\tau/T_1)}{1 - (1-X) \exp(-\tau/T_1)}, \quad (2)$$

representing the steady-state situation in which the decrease in amplitude during a pulse equals the increase in amplitude between pulses. Then a plot of  $\ln(M_n - M_\infty)$  vs  $n$  has an intercept  $I = \ln(M_0 - M_\infty)$  and a slope  $S = \ln\{1 - (M_0/M_\infty)[1 - \exp(-\tau/T_1)]\}$ . These may be combined to give

$$T_1^{-1} = \tau^{-1} \ln[(1 + M_\infty e^{-I}) / (1 + M_\infty e^{-I} e^S)], \quad (3)$$

$$X = (1 - e^S) / (1 + M_\infty e^{-I} e^S). \quad (4)$$

If desired for accuracy  $M_\infty$  may be determined independently by continuously running the pulses, i.e., separating both the sequences and the pulses in a sequence by  $\tau$ .

The conventional method of measuring  $T_1$  is to record the equilibrium FID amplitude, reached after many  $90^\circ$  pulses, as a function of pulse separation time,  $\tau$ . Then Eq. (2) applies with  $X=1$  giving  $M_\infty(\tau) = M_0(1 - e^{-\tau/T_1})$ , and a plot of  $\ln[M_0 - M_\infty(\tau)]$  vs  $\tau$  yields a straight line of slope  $-1/T_1$ . Note also that the effect of having  $\theta \neq 90^\circ$ , i.e.,  $X \neq 1$ , is seen from Eq. (2); the plot is no longer linear.

The rf tone-burst technique has advantages over the field tone burst in certain instances. If a metal probe is used, field modulation is limited by eddy currents to say 1 kHz, but the rf pulses, being applied to the transmitter coil, have a much higher maximum repetition rate. Also, a narrow linewidth, which may lead to resolution problems in the field modulation method,

gives a long FID after a pulse, allowing signal-to-noise improvement by narrow banding the detector. However, if the spin-spin relaxation time  $T_2$  is greater than  $2\tau$  care must be taken to exclude the contribution of spin echoes to the FID. (We have also observed echoes using the field modulation technique on a high-resolution instrument, a Varian A-60). This problem may be minimized by using small  $\theta$  and large  $\tau$ ,  $\tau < T_1$ .

In Fig. 1 are presented results of a pulse sequence in  $\text{Mn}^{2+}$ -doped  $\text{H}_2\text{O}$ . Here we set  $\tau = 25$  msec and calculate, from Eqs. (3) and (4),  $T_1 = 0.21$  sec and  $X = 0.33$  (or  $\theta = 48^\circ$ ). The  $T_1$  was checked by the usual  $90^\circ$ - $90^\circ$  pulse method [Eq. (2) with  $X=1$ ] and found to be within 10% of the stated value.

<sup>1</sup>D. C. Look and D. R. Locker, Phys. Rev. Letters **20**, 987 (1968).

### De-excitation Cross Section of $(\text{NO}^+)^*$ in $\text{NO}^\dagger$

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(Received 17 October 1968)

The quantitative study of the collision properties of ions in long-lived excited states is only beginning, and as yet few measurements of any of the cross sections for reactions involving ions of this type have been reported. Recently, a method was developed for determining the relative fractional abundances of the ground- and the aggregate excited-state ions present in an ion beam.<sup>1</sup> When this technique was applied to an  $\text{NO}^+$  ion beam,<sup>2</sup> it was found that the fraction of excited ions in the beam was dependent upon the pressure in the ion source. This pressure dependence has been used in the present work to determine the cross section for the de-excitation of excited  $\text{NO}^+$  during collisions with neutral  $\text{NO}$  at nearly thermal energy.

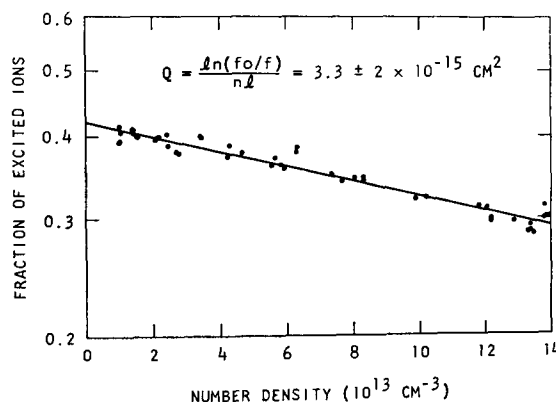


FIG. 1. Semilogarithmic plot of the fraction of excited ions as a function of number density.